#### Inorganica Chimica Acta 365 (2011) 220-224

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



# Reactions and structures in the gallium(III)/indium(III)-N,N-dimethylthioformamide systems

## Önder Topel<sup>1</sup>, Ingmar Persson<sup>\*</sup>, Daniel Lundberg, Ann-Sofi Ullström

Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden

#### ARTICLE INFO

Article history: Received 20 March 2010 Received in revised form 1 September 2010 Accepted 10 September 2010 Available online 17 September 2010

Keywords: Gallium(III) Indium(III) N,N-dimethylthioformamide (DMTF) EXAFS

#### ABSTRACT

The structure of the *N*,*N*-dimethylthioformamide (DMTF) solvated gallium(III) ion has been determined in solution by means of extended X-ray absorption fine structure (EXAFS) spectroscopy. The gallium(III) ion is four-coordinate in tetrahedral fashion with a mean Ga–S bond distance of 2.233(2) Å in DMTF solution. At the dissolution of indium(III) perchlorate or trifluoromethanesulfonate in DMTF coordinated solvent molecules are partly reduced to sulfide ions, and a tetrameric complex with the composition  $[In_4S_4(SHN(CH_3)_2)_{12}]^{4+}$  is formed. The structure of the solid tetrameric complex in the perchlorate salt was solved with single crystal X-ray diffraction. Four indium(III) ions and four sulfide ions form a highly symmetric heterocubane structure where each indium binds three bridging sulfide ions and each sulfide ion binds three indium(III) ions with a mean In–S bond distance of 2.584(1) Å, and S–In–S angles of 90.3(1)°. Each indium(III) additionally binds three DMTF molecules at significantly longer mean In–S bond distance, 2.703(1) Å; the S–In–S angles are in the range 80.3–90.4°. Large angle X-ray scattering data on a DMTF solution of indium(III) trifluoromethanesulfonate show that the same tetrameric species characterized in the solid state is also present in solution, whereas the EXAFS measurements only give information about the In–S bond distances due to the short core hole lifetime.

© 2010 Elsevier B.V. All rights reserved.

#### 1. Introduction

The number of homoleptic gallium(III) and indium(III) complexes with sulfur donor ligands is limited, and no pure solvate complexes with monodentate sulfur donor solvents have been reported so far. The homoleptic complexes of gallium(III) and indium(III) with monodentate sulfur donor ligands are all thiolates, and have all tetrahedral configuration with mean Ga-S and In-S bond distances of 2.268 and 2.462 Å, respectively, Tables S1 and S2. The homoleptic complexes with bidentate sulfur donor ligands as xanthates, carbamates and dithiophosphates, have octahedral configuration with mean Ga-S and In-S bond distances of 2.437 and 2.603 Å, respectively, Tables S1 and S2. Both gallium(III) and indium(III) have ability to form metal-sulfur clusters, including tetrameric cubane-like M<sub>4</sub>S<sub>4</sub> complexes where the metal additionally binds one organic group or a soft ligand with distorted configuration around the metal ion. The mean Ga-S and In-S bond distances in these tetrameric structures are 2.360 and 2.557 Å, respectively, and with M-S-M and S-M-S angles somewhat below and above 90°, respectively, Tables S1 and S2. No tetrameric heterocubane structures with octahedral configuration around the metal ion

\* Corresponding author.

have been reported so far, and only one, with a  $Ga_4S_4$  core, has ordinary electron-pair donor ligands binding to the metal ions.

*N*,*N*-dimethylthioformamide is a polar sulfur donor solvent with high dipole moment,  $\mu$  = 4.44 D, and relative permittivity,  $\varepsilon$  = 47.5 [1]. This means that most salts have high solubility and are highly dissociated in DMTF, an unusual property for a sulfur donor solvent. Another interesting feature of DMTF is the well-ordered bulk structure due to its hydrogen bonding ability; DMTF forms stronger internal hydrogen bonds than its oxygen analog N,N-dimethylformamide [1]. DMTF is a strong electron-pair donor solvent with soft Lewis base character,  $D_{\rm S}$  = 52 [2], and solvates soft metal ions such as gold(I) and silver(I) very well, while hard metal ions as sodium and potassium are weakly solvated [3]. The structural studies of DMTF solvated metal ions in solution often show low symmetry due to electronic effects as shown for silver(I) and mercury(II), and that in the case of gold(I) and mercury(II) the coordination number is lower, two and four, respectively, than sterically possible [4,5]. The solvation of the zinc(II), cadmium(II), mercury(II), copper(I), silver(I), gold(I), iron(II) and iron(III) ions has been studied in DMTF solution by EXAFS, LAXS, transfer thermodynamics and vibrational spectroscopy [3-7].

In this study, we report the structure of the DMTF solvated gallium(III) ion in DMTF solution, and the structure of the reaction product of indium(III) and DMTF, a novel highly symmetric tetramer with cubane configuration, where the indium(III) ions octahedrally bind three sulfide ions and three DMTF molecules,



E-mail address: ingmar.persson@kemi.slu.se (I. Persson).

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, Faculty of Arts and Sciences, Akdeniz University, 07058 Antalya, Turkey.

in both solid state and solution as studied by single crystal X-ray diffraction, large angle X-ray scattering (LAXS) and extended X-ray absorption fine structure (EXAFS).

## 2. Experimental

## 2.1. Chemicals

*N*,*N*-dimethylthioformamide was prepared by reacting phosphorus pentasulfide (Merck) and *N*,*N*-dimethylformamide (Merck) in benzene, according to a procedure given by Gutmann et al. [8], or purchased (Aldrich), and purified by distillation at reduced pressure prior to use.

Anhydrous gallium(III) and indium(III) trifluoromethanesulfonate,  $M(CF_3SO_3)_3$ , (M = Ga or In), were prepared by adding an excess trifluoromethanesulfonic acid,  $CF_3SO_3H$  (Fluka), dropwise to aqueous slurries of gallium(III) oxide,  $Ga_2O_3$  (Fluka) and indium(III) hydroxide,  $In(OH)_3$  (Fluka). The slurries were refluxed for 2 h until a clear solution was obtained. The solutions were filtered, and water and excess acid were boiled off at ca. 450 K. The anhydrous gallium(III) and indium(III) trifluoromethanesulfonates were stored in oven at ca. 450 K to avoid uptake of water.

Indium(III) perchlorate hexahydrate (Alfa) was dissolved in a minimum amount of dry acetone and then shaken for a few minutes. 2,2-Dimethoxypropane (Merck) was added to eliminate the water of the hydrate [9], and after shaking the mixture for ca. 15 min, six equivalents of DMTF were added to the reaction mixture. As soon as the mixture was shaken a yellowish-white precipitate was formed, **1**. This mixture was put in freezer where colorless single crystals suitable for X-ray studies were formed. The yield of this reaction is almost complete. The melting point is 439±1 K, but the compound turned brownish at ca. 403 K. The infrared spectrum of **1** is given in Fig. S1, suspended in oil and hexachlorobutadiene.

It was not possible to get any crystals of the DMTF solvated gallium(III) perchlorate or trifluoromethanesulfonate even though several methods were attempted. However, when the same method as for indium was applied on gallium, an interesting absorption in UV–Vis was observed. The color of the solution was purple under a mercury lamp, while it was reddish in daylight.

#### 2.2. Solutions and crystals

The DMTF solutions of gallium(III) and indium(III) trifluoromethanesulfonate for EXAFS and LAXS studies were prepared by dissolving respective anhydrous salt in freshly distilled DMTF; the composition of these solutions are summarized in Table 1. The yellow powder obtained by evaporation of the solvent from the DMTF solution of indium(III) perchlorate was studied by means of EXAFS.

## 2.3. Extended X-ray absorption fine structure measurements

Gallium and indium *K* edge X-ray absorption data were obtained at beam-line 4-1 at Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA. The beam-line was equipped with Si[220] double crystal monochromator. The storage ring at SSRL operated at 3.0 GeV and a maximum current of 100 mA. Data collection at the gallium *K* edge was carried out in transmission and fluorescence mode simultaneously, using ion chambers with a flow of a gas mixture of helium and nitrogen, and a Lytle detector [10] filled with argon gas. Higher order harmonics were rejected by detuning the second monochromator crystal to 50% of maximum intensity at the end of the scan. Data collection at the indium *K* edge was only carried out in transmission mode, using ion cham-

#### Table 1

Concentrations (mol dm $^{-3}$ ) of *N*,*N*-dimethylthioformamide (DMTF) solutions used in EXAFS or LAXS measurements.

Sample	Concentration (mol dm <sup>-3</sup> )	State	Method
Ga(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> in DMTF In(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> in DMTF In(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> in DMTF [In <sub>4</sub> S <sub>4</sub> (C <sub>3</sub> H <sub>7</sub> SH) <sub>12</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	1.35 1.00 0.763	Solution Solution Solution Yellow powder	EXAFS EXAFS LAXS EXAFS

bers with a flow of a gas mixture of nitrogen and argon. The second monochromator crystal was detuned to 80% of maximum intensity to reject higher order harmonics. The solutions were kept in cells with Mylar tape windows and a Teflon spacer 1–2 mm thick. The solids were ground to a homogeneous mixture with an appropriate amount of boron nitride (BN) to reach an intensity step of unity, and placed in a 1.5 mm aluminium frame with Mylar tape windows. Energy calibration of the X-ray absorption spectra was performed by simultaneously recording the edge spectrum of a metallic gallium or indium foil during the data collection, and assigning the first K edge inflection point to 10368.2 and 27940.0 eV, respectively [11]. After energy calibration, 2–3 scans were averaged for each sample. The EXAFSPAK program package was used for the data treatment [12]. The EXAFS oscillations were extracted using standard procedures for pre-edge subtraction, spline removal and data normalization. Model fitting, including both single and multiple back-scattering pathways, was performed with theoretical phase and amplitude functions calculated ab initio by means of the computer code FEFF7 [13]. The  $k^3$ -weighted EXAFS oscillation was analyzed by a non-linear least-squares fitting procedure of the model parameters.

## 2.4. Single crystal X-ray diffraction

Data collection were performed on a Bruker SMART platform equipped with a CCD area detector [14] and a graphite monochromator using Mo K $\alpha$  radiation,  $\lambda = 0.7107$  Å, at room temperature. A hemisphere data with 1271 frames was collected using the omega scan method. The crystal to detector distance was 5.0 cm. The first 50 frames were re-measured at the end of the data collection to check crystal and instrument stability, no absorption correction was applied. The structure was solved by direct methods in SHELXTL [15], and refined using full-matrix least squares on  $F^2$ . Nonhydrogen atoms were treated anisotropically. Hydrogen atoms were calculated in ideal positions riding on their respective carbon atom.

#### 2.5. Large-Angle X-ray Scattering (LAXS)

A large-angle  $\theta - \theta$  diffractometer was used to measure the scattering of Mo K $\alpha$  radiation,  $\lambda$  = 0.7107 Å, on the free surface of the N,N-dimethylthioformamide solution of indium(III) trifluoromethanesulfonate. The solution was contained in a Teflon cup inside a radiation shield with beryllium windows. The scattered radiation was monochromatized of by means of a focusing LiF crystal. The intensity was measured at 450 discrete points in the range  $0.5 < \theta < 65.0^{\circ}$  (2 $\theta$  is the scattering angle). A total amount of 100 000 counts was accumulated at each angle and the whole angular range was scanned twice, corresponding to a statistical uncertainty of about 0.3%. The divergence of the primary X-ray beam was limited by 1 or  $1/4^{\circ}$  slits for different  $\theta$  regions with overlapping some part of data for scaling purposes. All data treatment was carried out by using of the KURVLR program [16] described more in detail elsewhere [5]. The experimental intensities were normalized to a stoichiometric unit of volume containing one indium



**Fig. 1.** Representation of the heteroatomic In–S cage of  $[In_4S_4(C_3H_7NS)_{12}](CIO_4)_4$ . Thermal ellipsoids are set to 50%, and all symmetry-equivalent atoms in the heterocubane complex are included. For purposes of clarity, hydrogen atoms have been excluded, and three of the indium(III) ions have partially transparent DMTF ligands.

## Table 2

Crystallographic data on solid  $[In_4S_4(C_3H_7NS)_{12}](ClO_4)_4$  at room temperature.

	$[In_4S_4(C_3H_7NS)_{12}](ClO_4)_4$
Formula	$C_{36}H_{84}Cl_4 In_4N_{12}O_{16}S_{16}$
Molecular weight	2055.19
Crystal system	tetragonal
Space group	I-42 m (No. 121)
a (Å)	18.1125(15)
b (Å)	18.1125(15)
<i>c</i> (Å)	12.1492(11)
α (°)	90
β (°)	90
γ (°)	90
V (Å <sup>3</sup> )	3985.7(6)
T (K)	298(2)
Ζ	2
$\rho_{\rm calc}  ({ m g}  { m cm}^{-3})$	1.712
$\mu$ (mm <sup>-1</sup> )	1.755
Crystal size (mm)	$0.59 \times 0.45 \times 0.44$
$\theta$ Range (°)	1.59-25.02
Index ranges	$-18 \leqslant h \leqslant 22$ , $-22 \leqslant k \leqslant 20$ ,
	$-14 \leqslant l \leqslant 14$
Measured reflections	10 872
Unique reflections (R <sub>int</sub> )	1878 (0.0279)
Refinement method	full-matrix least-squares on F <sup>2</sup>
Final $R_1$ , $wR_2 [I > 2s(I)]^a$	0.0306, 0.0815
	0.0335, 0.0845 (all data)
Absolute structure parameters	0.06(3)
Largest difference in peak (e/Å <sup>-3</sup> )	0.743
Largest difference in hole (e $/Å^{-3}$ )	-0.428

<sup>a</sup> *R* values are  $\overline{f_c^2} = \sqrt{\frac{1}{2} \left[ w(F_0^2)^2 \right]}^{0.5}$ . defined as  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \sum |F_o|, wR_2 = \left[ \sum |w(F_o^2 - F_c^2)| / \sum \left[ w(F_o^2)^2 \right] \right]^{0.5}$ .

atom, using the scattering factors *f* for neutral atoms, including corrections for anomalous dispersion,  $\Delta f'$  and  $\Delta f''$  [17], and values for Compton scattering [18]. To receive a better alignment of the intensity function, a Fourier back-transformation was applied to eliminate spurious not related to any interatomic distances peaks below 1.2 Å in the radial distribution function [19]. Least-squares refinements of the model parameters were performed by means of the STEPLR program [20] to minimizing the error square sum  $U = \sum w(s)[i_{exp}(s) - i_{calc}(s)]^2$ , where w(s) is a weighting factor.

#### Table 3

Selected bond distances and angles from the crystal structure determination of solid
[In <sub>4</sub> S <sub>4</sub> (C <sub>3</sub> H <sub>7</sub> NS) <sub>12</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ; S1 and its symmetry-related counterpart S1' are sulfide
sulfurs, while S2 and S3 are N,N-dimethylthioformamide sulfurs.

Bond	R (Å)	Angle	(°)
In1–S1	2.594(1)	S1-In1-S1	90.36(4)
In1-S1′	2.563(2)	S1-In1-S1'	90.30(4)
In-S <sub>mean</sub> (in cube)	2.584(1)		
In1–S2	2.720(1)	S1-In1-S3	89.28(4)
In1–S3	2.669(2)	S2-In1-S2	80.27(6)
		S2-In1-S3	88.47(4)
In-S <sub>mean</sub> (terminal)	2.704(1)		
		S1-In1-S2	174.51(4)
		S1-In1-S3	179.48(5)
		In1-S2-C2	97.4(2)
		In1-S3-C3	105.1(3)
In-S <sub>mean overall</sub>	2.644(1)		

#### Table 4

Bond distances, d (Å), Debye–Waller factors,  $\sigma^2$  (Å<sup>2</sup>), and number of distances, n, for the DMTF solvated the gallium(III) and  $[In_4S_4(C_3H_7NS)_{12}]^{4+}$  in solid and solution as determined by EXAFS and LAXS at room temperature;  $E_o$  (eV) is the refined threshold energy and  $S_o^2$  is refined amplitude reduction factor.

Sample	n	d	$\sigma^2$	Eo	$S_o^2$
$Ga(CF_3SO_3)_3$ in solution, EXAFS					
Ga-S	4	2.233(1)	0.0124(2)	10373.8(2)	1.04(2)
Ga…C	4	3.052(7)	0.014(1)		
Ga-S-C	8	3.44(1)	0.010(2)		
Ga-S-S	12	4.123(7)	0.0055(9)		
Ga-S-Ga-S	4 + 12	4.48(2)	0.015(4)		
Solid $[In_4S_4(C_3H_7NS)_{12}](ClO_4)_4$ , EXAFS					
In-S <sub>S</sub>	3	2.568(3)	0.0040(4)	27946.1(2)	0.84(2)
In-S <sub>DMTF</sub>	3	2.661(3)	0.0044(5)		
In…C	3	3.487(6)	0.0064(6)		
In-S-C	6	3.67(2)	0.011(4)		
$[In_4S_4(C_3H_7NS)_1]$	<sub>2</sub> ] <sup>4+</sup> in solu	tion, EXAFS			
In-S <sub>S</sub>	3	2.576(5)	0.0047(4)	27946.0(2)	0.87(2)
In-S <sub>DMTF</sub>	3	2.658(3)	0.0061(5)		
In…C	3	3.424(8)	0.0101(10)		
In-S-C	6	3.68(1)	0.030(12)		
$[In_4S_4(C_3H_7NS)_{12}]^{4+}$ in solution, LAXS					
In-S	3	2.619(4)	0.0100(3)		
In…In	1.5	3.622(3)	0.0226(6)		
InS	4	4.546(5)	0.0277(9)		
In…S	6	5.837(4)	0.0175(5)		
In…C	3	3.353(9)	0.025(3)		

#### 3. Results and discussion

## 3.1. The dodecakis(N,N-dimethylthioformamide)tetrasulfidotetraindium(III) ion

Dodecakis(N,N-dimethylthioformamide)tetrasulfidotetraindium(III) perchlorate, 1, [In<sub>4</sub>S<sub>4</sub>(SCHN(CH<sub>3</sub>)<sub>2</sub>)<sub>12</sub>](ClO<sub>4</sub>)<sub>4</sub>, crystallizes in the tetragonal space group I-42 m (No. 121). The structure of the  $[In_4S_4(SCHN(CH_3)_2)_{12}]^{4+}$  ion is a highly symmetric heterocubane with four indium(III) and four sulfide ions forming an almost regular cube with each indium binding to three sulfide ions and each sulfide ion to three indium(III) ions. The In-S bond distances within the cube are 2.5633(14) and 2.5942(9)Å, and the  $S_s$ -In- $S_s$ angles are 90.30(4) and 90.36(4)°. Each indium(III) ion additionally binds three DMTF molecules at 2.6693(18) and 2.7198(12) Å completing an almost regular octahedral configuration around indium with S<sub>DMTF</sub>-In-S<sub>DMTF</sub> angles of 89.28(4) and 80.27(6)°, and In-S-C angles of 97.4(3) and 105.1(3)°, Fig. 1. The mean In-S bond distance in **1** is 0.02 Å longer, and the S–In–S angle much more close to 90° than in the reported In<sub>4</sub>S<sub>4</sub> clusters where the indium(III) ion binds only one more additional group, Table S2. The In-S-In angle is on the other hand somewhat smaller than in other reported In<sub>4</sub>S<sub>4</sub> clusters. The perchlorate ion is disordered, and two positions of the crystallographic independent oxygen atoms O1 and O2 were refined with each set reaching occupancies of 47% and 53%, respectively. Crystallographic data and selected bond distances and angles in 1 are given in Tables 2 and 3.

LAXS data on a concentrated indium(III) trifluoromethanesulfonate solution in DMTF, 0.763 mol dm<sup>-3</sup>, confirms the presence of a tetrameric complex almost identical to that described in the solid state above. The mean In–S bond distance is 2.62(1) Å, and the mean In…In distance 3.62(1) Å, which is in full agreement with distances in **1**. The strong contributions at 4.55(1) and 5.84(1) Å correspond to In…S distances, Table 4, showing beyond any doubt that the dominating species is the tetramer as these peaks should not be present if a monomeric solvated indium(III) ion had been the dominating one. The fit of LAXS data are given in Fig. 2, and the refined structure parameters in Table 4. The EXAFS spectra of **1** and the DMTF solution of indium(III) trifluoromethanesulfonate are identical (Fig. 3). Due to the short core hole life time, the



**Fig. 2.** (Top) LAXS radial distribution curves for a 0.763 mol dm<sup>-3</sup> *N*,*N*-dimethylthioformamide solution of indium(III) trifluoromethanesulfonate. Upper part: Separate model contributions (offset: 40) of the *N*,*N*-dimethylthioformamide solvated indium(III) ion (black line), the trifluoromethanesulfonate ion (light grey line) and *N*,*N*-dimethylthioformamide molecule (grey line). (Middle) Experimental RDF: D(r)- $4\pi r^2 r_0$  (solid line); sum of model contributions (grey line); difference (light grey line). (Bottom) Reduced LAXS intensity functions *si*(*s*) (black thin line); model *si*<sub>calc</sub>(*s*) (thick grey line).

information beyond the first scattering shell is very limited and uncertain. (*cf.* Fig. 4) However, it was possible to resolve two different In–S bond distances, In–S<sub>S</sub> = 2.57(1) and In–S<sub>DMTF</sub> = 2.66(1) Å, which is in good agreement with the crystallographic data for **1** (Tables 3 and 4).

Dodecakis(*N*,*N*-dimethylthioformamide)tetrasulfidotetraindium(III) perchlorate, **1**, is novel in three respects: it is the first (Ga/In)<sub>4</sub>S<sub>4</sub> cluster with an octahedral configuration around the metal ion, the first (Ga/In)<sub>4</sub>S<sub>4</sub> cluster with simultaneous sulfur electron-pair donor binding to the metal ion, and the first In<sub>4</sub>S<sub>4</sub> cluster with an electron-pair donor binding to the metal. Previously, only one Ga<sub>4</sub>S<sub>4</sub> complex with an electron-pair donor ligand binding to the metal has been reported,  $[Ga_4S_4(NC_9H_{18})_4]$  [21].

## 3.2. DMTF solvated gallium(III) ion

The EXAFS data on the DMTF solvated gallium(III) in solution give a mean Ga–S distance of 2.233(1)Å. The bond distances were modeled with main contributions from Ga–S and Ga…C single back-scattering, a three-leg back-scattering path within the Ga–S–C entity, and strong multiple scattering within the tetrahedral GaS<sub>4</sub> core. The structure parameters are summarized in Table 4



**Fig. 3.** Fit of the EXAFS data for (a) a 1.35 mol dm<sup>-3</sup> *N*,*N*-dimethylthioformamide solution of gallium(III) trifluoromethanesulfonate, (b) a 1.00 mol dm<sup>-3</sup> *N*,*N*-dimethylthioformamide solution of indium(III) trifluoromethanesulfonate and (c)  $[In_4S_4(C_3H_7NS)_{12}]^{4+}$  in solid state; black line experimental data, grey line calculated model function using the parameters given in Table 4.



**Fig. 4.** Fourier transforms for (a) a 1.35 mol dm<sup>-3</sup> *N*,*N*-dimethylthioformamide solution of gallium(III) trifluoromethanesulfonate, (b) a 1.00 mol dm<sup>-3</sup> *N*,*N*-dimethylthioformamide solution of indium(III) trifluoromethanesulfonate and (c)  $[In_4S_4(C_3H_7NS)_{12}]^{4+}$  in solid state; black line experimental data, grey line calculated model function using the parameters given in Table 4.

and the fit of the EXAFS data and the Fourier transform are shown in Figs. 3 and 4. According to the ionic radii given for the gallium(III) ion in four-, five- and six-coordination, the expected Ga–S bond distances should be 2.22, 2.30 and 2.37 Å, respectively, assuming that the sulfur radius is 1.75 Å [22,23]. The mean Ga–S bond distance for four-coordinate gallium(III) complexes with monodentate S-donor ligands in the literature are 2.268 Å, while the corresponding values for six-coordinate gallium(III) complexes with bidentate S-donor ligands is 2.437 Å, Table S1. The some longer Ga–S bond distance in the tetrathiolatogallate(III) complexes is probably a somewhat larger atomic radius of the sulfur atom in the thiolate ions than in DMTF. These results strongly indicate that the DMTF solvated gallium(III) ion is four-coordinate, most probably in tetrahedral fashion. The large Debye–Waller factor of the Ga–S distance, 0.0124(2)Å<sup>2</sup>, shows a wide distribution in the Ga–S distances maybe caused by steric restrictions. The Ga–S–C angle of 104.5°, estimated from Ga–S, Ga–S–C and Ga…C back-scattering paths within the Ga–S–C entity, is within the expected range [4–7].

#### Acknowledgements

We gratefully acknowledge the Swedish Research Council, and the Scientific and Technological Research Council of Turkey (TUBI-TAK) BIDEB-2214 research fellowship programme for financial support to Ö.T., the Department of Chemistry, Institute of Natural Sciences of Akdeniz University, Antalya, Turkey, for giving leaving permission to one of us (Ö.T.). Portions of this research were carried out beam-line 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL), a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program. SSRL is acknowledged for the allocation of beam time and laboratory facilities. M.Sc. O. Nikonova is acknowledged for assisting in the recording of the infrared spectra.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.011.

#### References

- H. Borrmann, I. Persson, M. Sandström, C.M.V. Stålhandske, J. Chem. Soc., Perkin Trans. 2 (2000) 393 (and references therein).
- [2] I. Persson, M. Sandström, P.L. Goggin, Inorg. Chim. Acta 129 (1987) 183.
- [3] H.D. Inerowicz, W. Li, I. Persson, J. Chem. Soc., Faraday Trans. 90 (1994) 2223.
- [4] C.M.V. Stålhandske, C.I. Stålhandske, I. Persson, M. Sandström, F. Jalilehvand, Inorg. Chem. 40 (2001) 6684.
- [5] C.M.V. Stålhandske, C.I. Stålhandske, M. Sandström, I. Persson, Inorg. Chem. 36 (1997) 3167.
- [6] C.M.V. Stålhandske, I. Persson, M. Sandström, E. Kamienska-Piotrowicz, Inorg. Chem. 36 (1997) 3174.
- [7] D. Lundberg, A.-S. Ullström, P. D'Angelo, I. Persson, Inorg. Chim. Acta 360 (2007) 1809.
- [8] V. Gutmann, K. Danksagmüller, O. Duschek, Z. Phys. Chem. Neue Folge (Frankfurt) 92 (1974) 199.
- [9] K. Starke, J. Inorg. Nucl. Chem. 11 (1959) 77.
- [10] The EXAFS Company, http://www.exafsco.com/products/3-grid-detector.html.
- [11] A. Thompson, D. Attwood, E. Gullikson, M. Howells, K.J. Kim, J. Kirz, J. Kortright, I. Lindau, P. Pianetta, A. Robinson, J. Scofield, J. Underwood, D. Vaughn, G. Williams, H. Winick, X-ray Data Booklet, second ed., Lawrence Berkeley National Laboratory, Berkeley, CA, USA, 2001.
- [12] G.N. George, I.J. Pickering, EXAFSPAK A Suite of Computer Programs for Analysis of X-ray Spectra, Menlo Park, CA, USA, 1993.
- [13] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, J. Phys. Rev. B 52 (1995) 2995.
- [14] Bruker, Bruker SMART and SAINT, Area Detector Control and Integration Software, Bruker Analytical X-ray Systems, Madison, WI, 1995.
- [15] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.
- [16] G. Johansson, M. Sandström, Chem. Scr. 4 (1973) 195.
- [17] International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, UK, 1974.
- [18] D.T. Cromer, J. Chem. Phys. 50 (1969) 4857.
- [19] H.A. Levy, M.D. Danford, A.H. Narten, Data Collection and Evaluation with an X-ray Diffractometer Designed for the Study of Liquid Structure, Technical Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge, TN, 1966.
- [20] M. Molund, I. Persson, Chem. Scr. 25 (1985) 197.
- [21] G. Linti, M. Buhler, H. Urban, Z. Anorg. Allg. Chem. 624 (1998) 517.
- [22] R.D. Shannon, Acta Crystallogr., Sect. A 32 (1976) 751.
- [23] D. Lundberg, The coordination chemistry of solvated metal ions in DMPU a study of a space-demanding solvent, Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden, 2006, Available at http://dissepsilon.slu.se/archive/00001072/.